Finally, we have found that the preparation of **3**, sparsely outlined by Mironov[4,16] (44% yield), is extremely capricious and requires many more manipulations than are described. A detailed, improved procedure appears below which can reliably be done on a 4-mol scale in 66% yield.

Experimental Section

^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer. In all cases $CDCl_3$ was used as the solvent with $CHCl_3$ (δ 7.27) as an internal reference. GC analyses were performed on a Varian 3700 instrument with N_2 as the carrier gas at 30 mL/min. Retention times and integrals were recorded on a Hewlett-Packard 3390 recording integrator. All reactions were done in flame-dried glassware under a N_2 atmosphere. Anhydrous Et_2O, Mg turnings, and ethyl bromide were Mallinckrodt AR grade and used as received. Propargyl alcohol was distilled from K_2CO_3, and THF was distilled freshly from sodium benzophenone ketyl.

3-(Trimethylsilyl)-2-propyn-1-ol (3). In a three-necked, 2-L, round-bottomed flask fitted with mechanical stirrer, addition funnel, and condenser were placed 97.4 g (4 mol) of magnesium turnings and 700 mL of anhydrous Et_2O. To the stirred suspension was added 436 g (300 mL, 4 mol) of ethyl bromide at such a rate as to maintain gentle reflux. The mixture was refluxed 1 h further after complete addition. After the Grignard solution was cooled in an ice bath, 80 g (83 mL, 1.43 mol) of propargyl alcohol was slowly added with external cooling. Upon complete addition, the ice bath was removed, and the mixture was stirred overnight, during which time it slowly solidified. The mass was cooled in an ice bath and treated dropwise with 435 g (508 mL, 4 mol) of trimethylsilyl chloride. After approximately 100 mL of Me_3SiCl was added, the mass disintegrated into a slurry, at which point the ice bath was removed and the slurry allowed to warm to room temperature for the remainder of the addition. A Liebig condenser was then attached, and the Et_2O was distilled out (boiling range 38–40 °C). The resulting solid was heated on a steam bath for 3 h and cooled to room temperature. The mixture was suspended in 400 mL of Et_2O, treated dropwise with 200 mL of 1 N H_2SO_4, and stirred for 2 h. The Et_2O layer was separated and washed with water (2 × 300 mL) and brine (1 × 300 mL). The aqueous layer was diluted with 800 mL of 1 N H_2SO_4 and extracted with Et_2O (2 × 400 mL), and the Et_2O extracts were washed with water (2 × 300 mL) and brine (1 × 300 mL). All Et_2O extracts were combined, dried (Na_2SO_4), and concentrated in vacuo. The residue was distilled at reduced pressure (capillary) to yield 160 g of a 57:43 mixture of **3** and the trimethylsilyl ether of **3**; bp 76–80 °C (24–30 mm). This mixture was divided in half and hydrolyzed in portions as follows. A solution of 78.1 g of the mixture in 340 mL of THF was treated with 40 mL of 1 N H_2SO_4. After the mixture was stirred for 5 min, 250 mL of NaH_2PO_4 buffer solution (pH 7.04) was added followed by sufficient saturated $NaHCO_3$ solution to neutralize the acid. The solution was extracted with Et_2O (3 × 200 mL), and the Et_2O extracts were washed with water (2 × 250 mL) and brine (1 × 250 mL). The combined Et_2O layers were dried ($MgSO_4$) and concentrated in vacuo. The residual liquids thus obtained from two identical hydrolyses were combined and distilled to afford 120 g [66% yield (lit.[4] yield 44%)] of **3**: bp 56 °C (7 mm); ^{1}H NMR δ 0.27 (s, 9 H), 1.6 (t, J = 6 Hz, 1 H), 4.28 (d, 2 H, J = 6 Hz).

(*E*)-3-(Trimethylsilyl)-2-propen-1-ol (2). In a three-necked, 1-L, round-bottomed flask fitted with a thermometer, addition funnel, and N_2 inlet was placed 136 mL (0.50 mol) of a 3.67 M solution of sodium bis(methoxyethoxy)aluminum hydride in toluene followed by 200 mL of anhydrous Et_2O. The solution was cooled to 0 °C on ice and treated dropwise with a solution of 40 g (0.312 mol) of **3** in 200 mL of Et_2O. Ten minutes after complete addition the ice bath was removed, and the reaction was complete (GC[6] monitoring) within 1 h. The reaction was quenched by the dropwise addition of 400 mL of 2 N H_2SO_4. The organic layer was separated and washed with water (2 × 200 mL) and brine (1 × 200 mL). The aqueous layer was extracted with Et_2O (2 × 300 mL), and all the Et_2O phases were combined, dried ($MgSO_4$), and concentrated in vacuo. The residual liquid was distilled to yield 34.5 g (85%) of **2**: bp 80–81 °C (40 mm); ^{1}H NMR δ 0.23 (s, 9 H), 1.5 (t, J = 6 Hz, 1 H), 4.22 (dd, J = 6, 4 Hz, 2 H), 5.93 (d, J = 18 Hz, 1 H), 6.23 (dt, J_d = 19 Hz, J_t = 4 Hz, 1 H).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1**, 33755-86-1; **2t**, 59376-64-6; **2c**, 62861-80-7; **3**, 5272-36-6; 3-(Me_3Si)-**3**, 50965-66-7; **4**, 2917-47-7; sodium bis(2-methoxyethoxy)aluminum hydride, 22722-98-1.

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(15) Apparently a complex containing three oxygen ligands and only one hydride is insufficiently reactive to reduce the triple bond. This may not be unique to SMEAH since an excess of hydride is usually required with $LiAlH_4$ also.

(16) **Note Added in Proof**: A similar procedure for the preparation of **3** has recently appeared: Brandsma, L.; Verkruisse, H. O. "Synthesis of Acetylenes, Allenes and Cumulenes"; Elsevier: Amsterdam, 1981; p 58.

Communications

Regioselective Photoisomerizations of Bridgehead Substituted Dibenzobarrelenes and Benzonorbornadienes. The Implication of Excited-State Secondary Deuterium Isotope Effects of Benzo–Vinyl Bridging

Summary: Replacement of a bridgehead hydrogen by deuterium in the title compounds leads to k_H/k_D values of 1.11–1.27 (cyclopropyl substitution disfavored); these effects are opposite to those seen with other substitutents (except bromine) and demand that bridged radicals such as **2** be formed reversibly or not at all.

Sir: Di-π-methane photorearrangements have long been considered to proceed in stepwise fashion via a pair of biradical intermediates.[1] When benzo–vinyl bridging is involved, the conversion to product has been formulated as the result of initial bond making to generate a cyclopropane moiety followed by cleavage of an alternate three-membered ring bond. Direct proof of the existence of two discrete intermediates such as **2** and **3** has been exceedingly difficult to obtain, although Schaffner and co-workers have presented ESR and IR evidence for the intervention of two biradical intermediates during the low-temperature photoisomerization of **1** (R = COC_6H_5) to **4**. The other plausible alternative is, of course, a direct light-induced 1,2 aryl shift within such systems to generate rearranged biradicals directly (e.g., **1** → **3** → **4**). We now

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(1) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 16.

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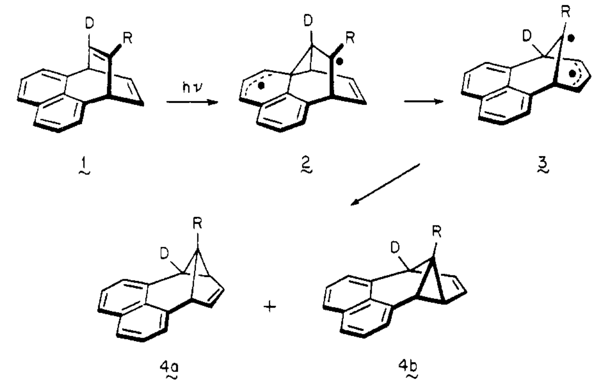
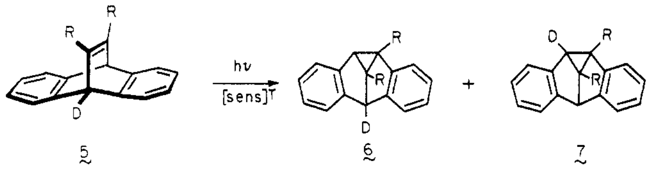


present evidence that requires that bridged biradicals such as **2** be formed reversibly or not at all.

Acetone-sensitized irradiation of dibenzobarrelene **5a**[3a] at 3000 Å proceeds regioselectively to give a 1.15:1 mixture of **6a** and **7a** in quantitative yield.[4] A k_H/k_D value greater than unity was determined by repeated integration of proton-decoupled ^{2}H NMR spectra of intact photoisomerization mixtures (4.38 ppm for **6a** and 3.73 ppm for **7a**). Analogous treatment of **5b**[3b] was seen to produce **6b** (3.78 ppm) and **7b** (2.40 ppm) in a ratio of 1.11.



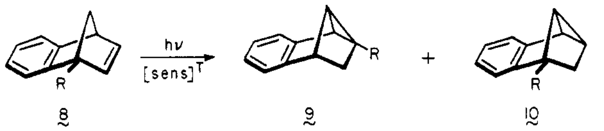
a, R = COOCH$_3$; b, R = H

The excited state behavior of a broader range of 1-substituted benzonorbornadienes (**8**) was also examined. The trimethylsilyl (**8d**),[5] methyl (**8f**),[5] and bromo derivatives (**8g**)[6] had been previously described. Access to the five additional compounds was most conveniently achieved via nucleophilic capture by the Grignard reagent: **8a**, $(CN)_2$;[7] **8b**, CO_2, then CH_2N_2; **8c**, $PhCO_3C(CH_3)_3$;[8] **8e**, H_2NOCH_3, then CH_3COCl, Et_3N;[9] **8h**, D_2O. Where these substrates are concerned, the irradiations were cleanly carried out in benzene solution with 3500-Å light in a Rayonet reactor with acetophenone as sensitizer.[4] The rearrangement product ratios and structural assignments given in Table I were determined from detailed ^{1}H NMR analysis of the isolated photoproducts.[10] An exception to this procedure was exercised in the case of **9h**/**10h**, where ^{2}H NMR analysis was once again utilized (2.21 and 3.58 ppm, respectively). The photoisomerization of **8h** was also performed in a 10 000 G magnetic field in order to investigate possible magnetic effects[11] on the regioselectivity of this di-π-methane rearrangement. Expectedly,[12] none was found (k_H/k_D = 1.27).[13]

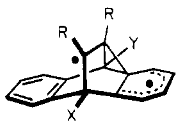
Table I. Bridging Regioselectivities for 1-Substituted Benzonorbornadienes (**8**)

R	**9**,[a] %	**10**,[a] %
8a, CN	100	0
8b, $COOCH_3$	100	0
8c, $OC(CH_3)_3$	100	0
8d, $Si(CH_3)_3$	100	0
8e, $NHCOCH_3$	100	0
8f, CH_3	90	10
8g, Br	50	50
8h, D	44	56

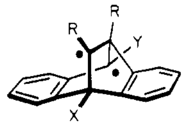
[a] The limits of detection are considered to be 3% except in the case of **8h** where it is ±0.4%.



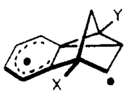
Substrates **5** and **8** were selected for study because they represent "doubly connected" di-π-methane substrates having too competitive bonding schemes open to them. We consider first the monodeuterated examples where pairs of isomeric products are formed via clean triplet processes that differ only in the involvement of the D- or H-substituted bridgehead carbon atoms. If the energy surfaces interconnecting the triplet states of **5** and **8** with their photoisomers contain no minima corresponding to **11** and **13**, the first discrete intermediates become **12** and **14**. Since recent studies by Adam and De Lucchi involving the denitrogenation of **15** have shown that diradicals of general structure **14** largely (>95%) prefer intramolecular cyclization to di-π-methane rearrangement,[14,15] arrival at this stage of the isomerization likely constitutes an irreversible commitment to product generation. The isotopic fractionation factors, which indicate that **12b** and **14b** are substantially favored over **12a** and **14a**, respectively, conform with observations by Crawford and Chang involving thermolysis reactions of 4-methylene-1-pyrazolines,[16] which



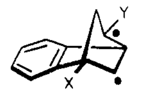
11a, X = H, Y = D
b, X = D, Y = H



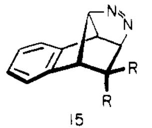
12a, X = H, Y = D
b, X = D, Y = H



13a, X = H, Y = D
b, X = D, Y = H



14a, X = H, Y = D
b, X = D, Y = H



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(2) (a) Demuth, M.; Lemmer, D.; Schaffner, K. *J. Am. Chem. Soc.* **1980**, *102*, 5407. (b) Demuth, M.; Bender, C. O.; Braslavsky, S. E.; Görner, H.; Burger, U.; Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1970**, *62*, 847.

(3) (a) Prepared by Diels–Alder addition of dimethyl acetylenedicarbonxylate to anthracene-*9-d*. The all-protio example is known: Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *486*, 191. (b) Prepared by cycloaddition of *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene to anthracene-*9-d* and subsequent treatment of the adduct with tetra-*n*-butylammonium fluoride in hot tetrahydrofuran [Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, 4643].

(4) No photoisomerization was seen in the absence of sensitizer.

(5) Ford, W. T. *J. Org. Chem.* **1971**, *36*, 3879.

(6) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1562. Chenier, P. J.; Jensen, S. R.; Jess, D. A.; Rosenblum, B. B. *Ibid.* **1973**, *38*, 4350.

(7) Grignard, V.; Bellet, E.; Courtot, C. *Ann. Chim.* **1915**, *4*, 28.

(8) Lawesson, S. O.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 4230.

(9) Brown, R.; Jones, W. E. *J. Chem. Soc.* **1946**, 781.

(10) Satisfactory combustion analytical and/or accurate mass spectral data have been obtained for all new compounds described herein.

(11) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *J. Am. Chem. Soc.* **1980**, *102*, 4843. Turro, N. J.; Mattey, J. *Ibid.* **1981**, *103*, 4200.

(12) The magnitude of the $^1S_0 \rightarrow {}^1T_0$ gap in diradicals that might be generated from **8**, although unknown, is believed to be large and at least several times the hyperfine splitting available at this field strength, thereby minimizing hyperfine induced intersystem crossing.

(13) Note the formula **10** is drawn in enantiomeric form for convenience.

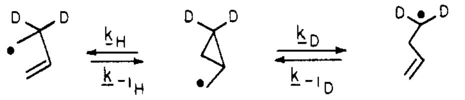
(14) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133.

(15) Compare: Zimmerman, H. W.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680.

(16) (a) Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837. (b) Chang, M. H.; Crawford, R. J. *Can. J. Chem.* **1981**, *59*, 2556.

reveal that the heavier isotope prefers to avoid the free-radical site. In other words, our observed k_H/k_D values are of suitable magnitude and in the proper direction to be accounted for in terms of a direct 1,2 aryl shift mechanism.

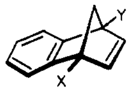
Alternatively, biradicals **11** and **13** might be true potential minima in their own right. Adherence by these systems to this mechanistic option would necessitate that the deuterium atom direct conversion preferentially to **11b** and **13b** so as to maintain itself away from the cyclopropyl site. One must now inquire whether the heavier isotope might be expected to exert secondary *kinetic* isotope effects of this magnitude in this direction. Since deuterium is well-known to exhibit a preference for sites richer in s character under equilibrium conditions,[17] the existence of an *equilibrium* isotope effect does not alone explain our findings. The source of the observed k_H/k_D values must consequently lie elsewhere. Some insight into this question has seemingly been provided by the research groups of Montgomery[18] and Ingold.[19] These workers have independently examined the interconversion of allylcarbinyl-d_2 radicals **16** and **17** via **18** and have implicated the ratio of **16**/**17** to be greater than unity, although unlikely to be larger than 1.2–1.3. The important point here is the fact that ring deuterated cyclopropylcarbinyl radicals prefer to undergo cleavage of that bond positioned between the unlabeled carbon centers. This being the case, intermediates **11a** and **13a** would be expected to return more often to starting material than **11b** and **13b** *if reversibility did prevail.* The higher concentration gradient of the latter pair of biradicals and their anticipated faster rate of conversion to **12b** and **14b** would explain the predominance of **6** and **10**.



16 18 17

If total advantage is to be directly taken of the radical stabilizing properties of R, *then the regioselectivities observed for **8a**–**8f** are more satisfyingly interpreted in terms of the first mechanistic option.* The lack of regioselectivity exhibited by **8g** may arise from the heavy atom effect of the bromine substituent or its relative inability to stabilize adjacent carbon-centered radicals.

Since the findings summarized herein demonstrate that the influence of bridgehead substitutents is clearly large, it is possible that pendant functional groups at each of the available sites exert their influence in a direct concerted manner.[20,21] At least three intriguing studies now become worthy of immediate attention. In the first, benzonorbornadienes that are differently substituted at the bridgehead sites as in **19** may serve as exceptionally sensitive probes of relative radical stabilization capabilities in the excited state. Direct competition experiments of this sort are unprecedented. Secondly, it becomes important to assess the relative controlling powers of bridgehead/aryl (**20**) and bridgehead/vinyl (**21**) substituent combinations. We hope to report on the outcome of these investigations in the near future.



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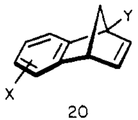

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Acknowledgment. We thank the National Science Foundation for financial support and Professor Matthew Platz for the use of instrumentation and helpful comments. The ^{2}H NMR spectra were obtained at the Ohio State University Chemical Instrument Center with the help of Dr. C. E. Cottrell.

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[17] (a) Paquette, L. A.; Kitching, W.; Heyd, W. E.; Meisinger, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 7371. (b) Goldstein, M. J.; Pressman, E. J. *Ibid.* **1981**, *103*, 6533 and references cited in these papers.

[18] Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 6556.

[19] Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

[20] (a) Paquette, L. A.; Cotttrell, D. M.; Snow, R. A.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3275. (b) Santiago, C.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *Ibid.* **1976**, *98*, 7443. (c) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723. (d) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977**, *99*, 3734. (e) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5972. (f) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5981. (g) Paquette, L. A.; Bay, E.; Ku, A. Y.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1982**, *47*, 422.

[21] (a) Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 7103. (b) Hahn, R. C.; Johnson, P. R. *Ibid.* **1977**, *99*, 1508.

[22] **Note Added in Proof.** Triptycene monodeuterated at the bridgehead position has been shown [Hemetsberger, H.; Neustern, F.-U. *Tetrahedron* **1982**, *38*, 1175] to undergo direct and sensitized photoisomerization with an isotope effect (k_H/k_D) of 2.2–2.4. On the basis of additional quantum yield studies, these authors have also concluded that the fractionation factor most likely stems from differences in reaction rate rather than from differences in radiationless deactivation.